Char Reactivities and Their Relationship to Pore Characteristics

S. Katta and D. L. Keairns
Westinghouse R&D Center
Pittsburgh, PA 15235

INTRODUCTION

The study of char reactivities is fundamental to the design and performance evaluation of gasifiers for coal gasification. This investigation was undertaken in connection with the development of the Westinghouse coal gasification process. The objective of the study was to determine the reactivities of several chars and to examine the relationship between the reactivities and the pore surface areas or mean pore diameters. If char reactivities can be predicted from pore surface area or pore mean diameter, char characterization becomes simpler. This method can then be used as a screening technique to assess the performance of gasifiers.

A detailed experimental investigation on the rate of carbon-steam ($C-H_2O$) and carbon-carbon dioxide ($C-CO_2$) reactions with coke breeze was reported by Katta and Keairns (1). The reactivities of chars were used to predict gasification rates in several pilot plant tests by means of a gasification model.

The reactivity of carbonaceous material in a H_2O or CO_2 atmosphere depends on the rank of coal, the rate of heating, and the heat treatment temperature, all of which influence the pore characteristics. The pore structure and the chemical nature of the char control the reactivity in a H_2O, CO_2, or oxygen atmosphere. The reactivity of a material may not be the same in all these atmospheres since the mineral content influences each of these reactions to a different extent and the same pores are not involved in these reactions. Information from the literature indicates that a limited understanding has been gained on the influence of different parameters on the reactivities of chars.

In any coal gasification process much of the carbon conversion takes place through a $C-H_2O$ reaction. Hence, it is important to establish char reactivities in a steam atmosphere rather than in other atmospheres. A study of char reactivities in the atmospheres of H_2O, CO_2, oxygen, and hydrogen is important for a fundamental understanding of char behavior.

Jenkins et al. (2) studied the reactivities of various chars in air at 500°C as a function of heat treatment temperature, mineral content, and pore structure. They found that the chars became less reactive as the heat treatment temperature was increased, and that the magnitude of the effect depended on the type of char. They observed, also, that the

level of transitional porosity (estimated from nitrogen adsorption) increases the reactivity markedly since the ability of a gaseous reactant to reach the surface area in the micropores is enhanced. They concluded that the reactivity of chars prepared at the same temperature and heating rate is predominantly influenced by mineral matter and the rank of the parent coal.

The reactivities of several chars in a CO_2 atmosphere and the changes in pore structure with carbon conversion were investigated by Dutta et al. (3). They found that almost the entire surface area of chars seemed to be due to micropores smaller than 0.01 to 0.02 μm in diameter. They concluded that the reactivities were almost proportional to the surface areas occupied by pores above about 0.003 μm in diameter, suggesting that smaller pores are inaccessible to gaseous reactant. They derived a rate equation with a parameter that represents the change in available pore surface area with carbon conversion.

Johnson (4) conducted a comprehensive study on the effects of physical and chemical properties of chars on their reactivities. He concluded that the gasification of chars with hydrogen and steam-hydrogen (H_2O-H_2) mixtures occurs primarily on the surface within micropores which were defined as less than 5.5 nm in diameter.

EXPERIMENTAL WORK

The reactivities of various chars were determined at a temperature of 927°C and a pressure of 10 atmospheres in a steam-hydrogen-nitrogen (H_2O-H_2-N_2) atmosphere. Experiments were conducted in a reactor of 3.5 cm id and 30.5 cm height which was heated externally by an electric furnace. A sample of about 35 g of char of -1.0 + 0.25 mm size was placed on the distributor and fluidized by the gaseous mixture. Gas samples were taken for different inlet gas compositions, and the reaction rate was determined from the product gas composition and the estimated amount of carbon present in the bed at the time the sample was taken. At the end of the test, the bed material was weighed and the product gas line flushed to collect fines. The amount of fines collected in any run was very small. A detailed description of the apparatus and the experimental procedure are given in reference (1). The reaction data were analyzed on the basis of the rate equation derived from Ergun's model (5).

CHAR PREPARATION

Renton, Minnehaha, and Montour chars were prepared in the Westinghouse process development unit. Western Kentucky and Utah chars were obtained from FMC Corporation and Synthane char from the Synthane pilot plant.

SURFACE AREA MEASUREMENT

We degassed the char samples at 110°C for about four hours prior to measuring their surface areas, using carbon dioxide as the adsorbate at 298 K on a micromeritics Model 2100 surface area analyzer. An equilibration time of about 30 minutes was allowed for each adsorption point. The molecular area of CO_2 at 298 K was taken as 25.3 $\AA^2$.

The Dubinin-Polanyi equation (D-P equation) was used for the evaluation of surface areas of chars and is given below:

$$\log V_a = \log V_o - D \log^2 (P_o/P_2) \quad (1)$$

A plot of log V_a versus $\log^2 (P_o/P_2)$ yields the value of log V_o from which the specific surface area of the sample can be calculated. A value of 63.5 atm was used for the saturation vapor pressure of CO_2 at 298 K.

PORE VOLUME MEASUREMENT

Measurements on pore volume were made with a Micromeritics mercury penetration porosimeter Model 910 series. Pressures up to 17,000 psi were used in these measurements to cover a pore diameter range of 100 to 0.0104 μm.

RESULTS AND DISCUSSION

The following rate equation for the coke breeze-H_2O reaction had been obtained in a previous study (1):

$$r_2 = k_2/(1 + P_{H_2}/K_2 P_{H_2O}) \quad (2)$$

where r_2, k_2, and K_2 are the reaction rate per unit mass, min^{-1}, the reaction constant, and the equilibrium constant, respectively. k_2 and K_2 are given by

$$k_2 = 4.85 \times 10^6 \cdot \exp(-48{,}200/RT) \quad (3)$$

$$K_2 = 2.25 \times 10^6 \cdot \exp(-42{,}600/RT) \quad (4)$$

where T is the absolute temperature in K. The rate data were plotted with P_{H_2}/P_{H_2O} versus the inverse reaction rate to obtain the reaction rate parameters. The intercepts on the ordinate and the abscissa give the values of K_2 and $1/k_2$, respectively. Results for Renton, Minnehaha, FMC Western Kentucky, Synthane, Montour, and Utah chars are shown in Figures 1 to 6. The initial relative reactivities of various chars with reference to coke breeze are given in Table 1.

Table 1

RELATIVE REACTIVITIES OF CHARS

Char	Rate Constant, k_2, min^{-1}	Initial Relative Reactivity	Surface Area by CO_2 Adsorption	Mean Pore Diameter, μm
Coke Breeze	0.008	1.00	13.9	0.196
Minnehaha	0.08	9.88	85.2	0.066
Renton	0.02	2.47	199.8	0.033
Utah	0.081	10.13	126.8	0.036
FMC Western Kentucky	0.095	11.73	117.9	0.041
Synthane*	0.08	10.67	63.2	0.068
Montour	0.0195	2.44	23.3	0.161

*Reactivity evaluated at 32 percent carbon conversion.

The initial relative reactivities of the chars were plotted versus the pore surface areas determined by CO_2 adsorption and interpreted by Dubinin-Polanyi equation in Figure 7. If the data on Renton char is excluded, a correlation of these two variables can be obtained. In the absence of reactivity data, the relative reactivity can be estimated from CO_2 surface areas. This method, however, will probably be uncertain for some materials whose surface area develops primarily after significant conversion. Work on additional chars is recommended in order to improve the reliability of the method and to establish limitations.

The mean pore diameter of chars is calculated from the relation $\bar{D} = 4V/S_{CO_2}$, where V is the pore volume as measured by means of mercury porosimeter and S_{CO_2} is the surface area as measured from CO_2 adsorption. The relative char reactivities were plotted versus the mean pore diameter in Figure 8. A linear correlation was obtained by a regression analysis after excluding the data on Renton char. Use of this correlation requires the measurement of surface area and pore volume. Figures 7 and 8 indicate that more reactive chars have greater surface areas and smaller mean pore diameters than others, as would be expected.

SUMMARY

Relative reactivities of chars in a H_2O-N_2-H_2 atmosphere were measured in a laboratory fluidized bed. Results were analyzed on the basis of Ergun's rate equation, and the relative reactivities were calculated with reference to coke breeze. Surface areas of chars were obtained by means of CO_2 adsorption, and pore volumes were measured by means of mercury penetration porosimetry. A correlation can be identified between the relative reactivity versus the surface areas and the mean pore diameter for the limited number of chars investigated in the present study. Additional studies should be conducted to establish the range of validity with additional chars and drawbacks of this approach.

ACKNOWLEDGEMENTS

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REFERENCES

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3. Dutta, S., Wen, C. Y. and Belt, R. J., Ind. Eng. Chem. Process Des. Dev., 16(1), 20-30 (1977).

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5. Ergun, S., Bureau of Mines Bulletin 598, Washington, D.C. (1962)

NOMENCLATURE

D	a constant
$\bar{D}$	mean pore diameter of chars
k_2	rate constant of carbon-steam reaction, min^{-1} as defined by Ergun's rate equation
K_2	equilibrium constant of carbon-steam reaction as defined by Ergun's theory
P_{H_2}, P_{H_2O}	partial pressures of hydrogen and steam, respectively
P_o	saturation vapor pressure of adsorbate at adsorption temperature
r_2	initial rate per unit mass of carbon-steam reaction, (corresponds to a carbon conversion of zero) min^{-1}
S_{CO_2}	surface area of chars measured by CO_2 adsorption
T	absolute temperature of char bed, K
V	pore volume, cm^3/g
V_a	amount of CO_2 adsorbed at equilibrium pressure P_2
V_o	micropore capacity
X	fractional carbon conversion

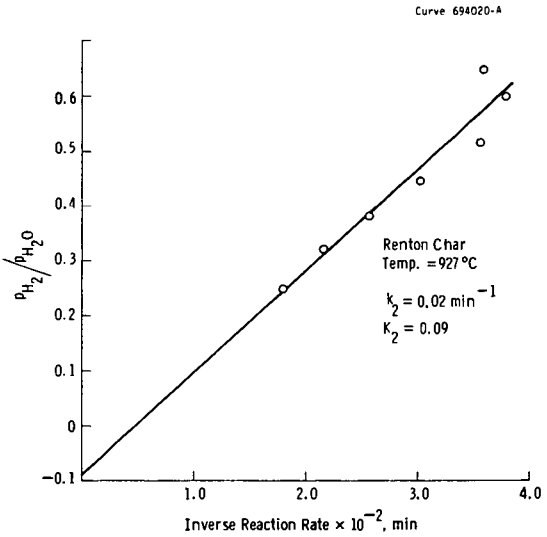

Figure 1 – Renton char – steam reaction

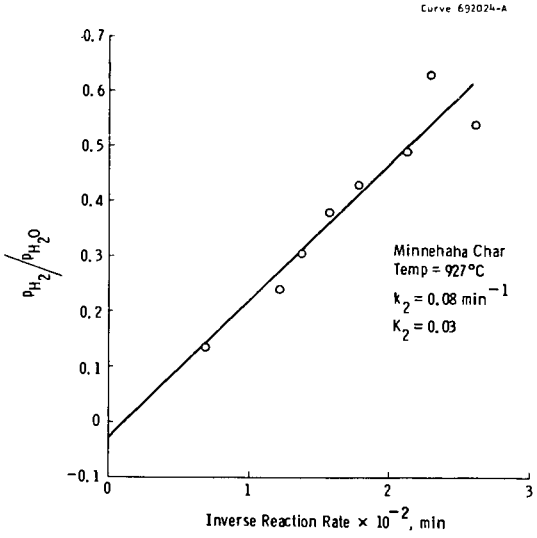

Figure 2 – Minnehaha char – steam reaction

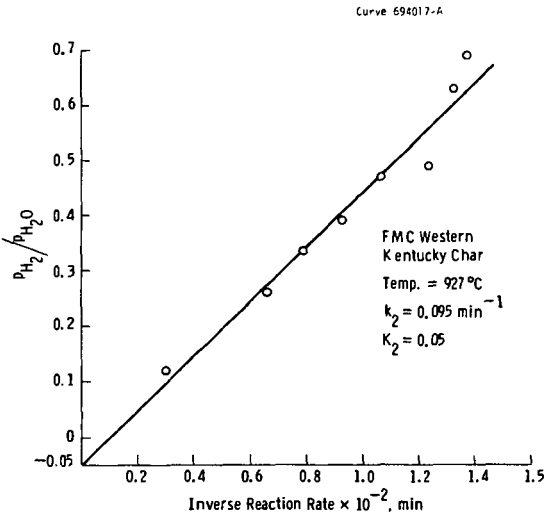

Figure 3 – FMC western Kentucky char – steam reaction

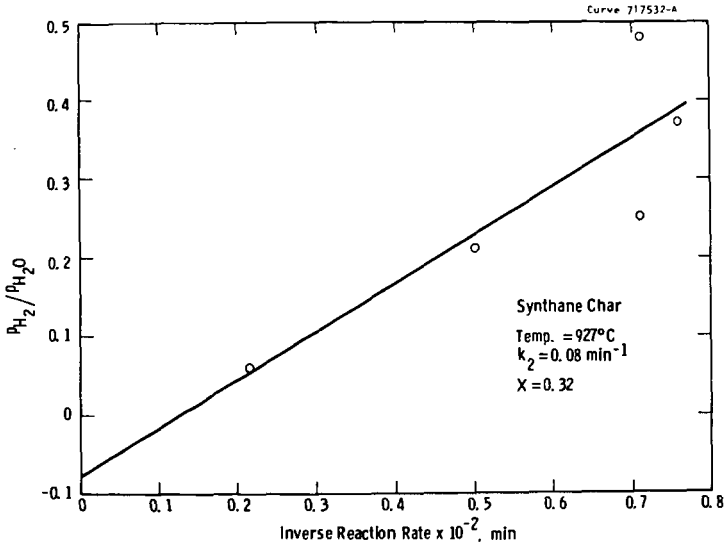

Figure 4 – Synthane char – steam reaction

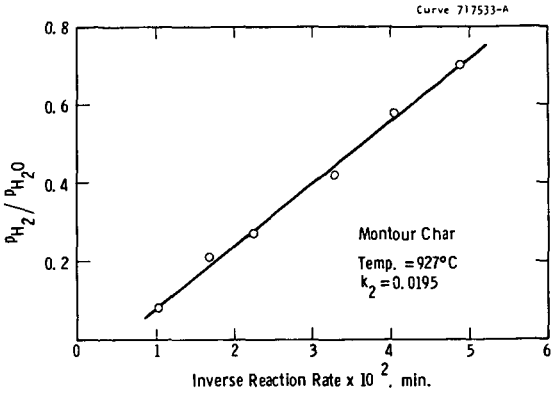

Figure 5 – Montour char – steam reaction

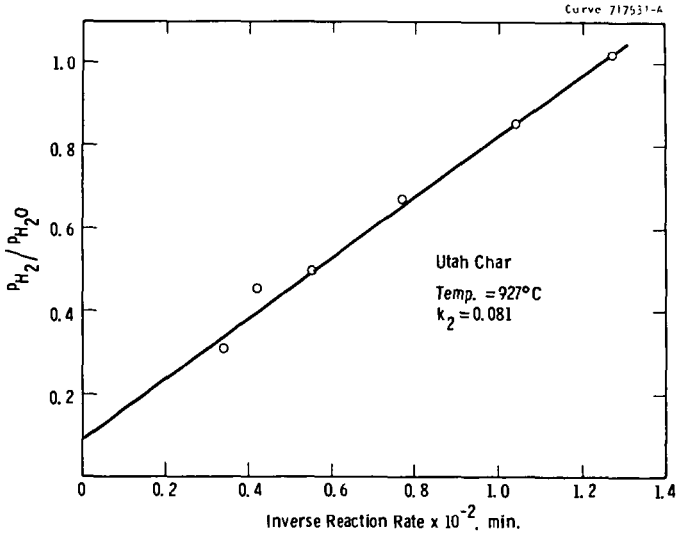

Figure 6 – Utah char – steam reaction

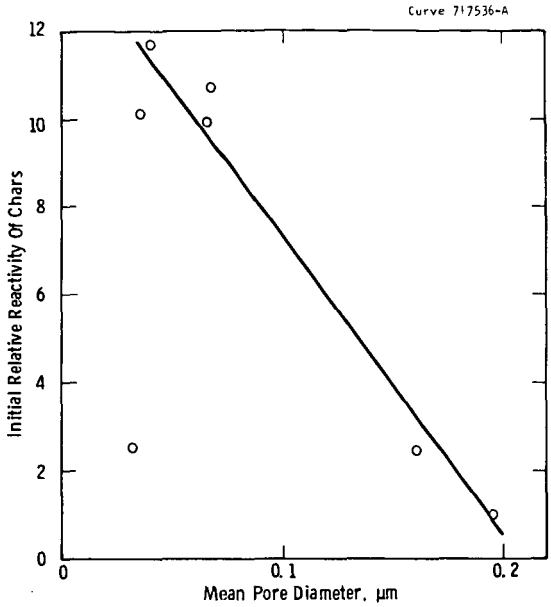

Figure 8 – Relationship between reactivity and mean pore diameter

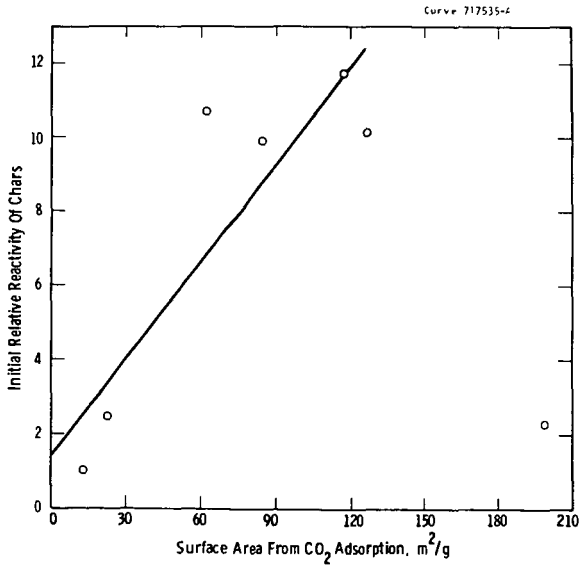

Figure 7 – Relationship between reactivity and surface area of chars